**Atmospheric
Chemistry
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Discussions**

# On the chemical nature of the oxygenated organic aerosol: implication in the formation and aging of $\alpha$-pinene SOA in a Mediterranean environment, Marseille

**I. El Haddad[1,*], B. D'Anna[2], B. Temime-Roussel[1], M. Nicolas[2], A. Boreave[2], O. Favez[2,**], D. Voisin[3], J. Sciare[4], C. George[2], J.-L. Jaffrezo[3], H. Wortham[1], and N. Marchand[1]**

[1]Aix-Marseille Univ., Laboratoire Chimie Environnement, 13331, Marseille cedex 03, France
[2]Université Lyon 1, Lyon, 69626, CNRS, UMR5256, IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Villeurbanne, 69626, France
[3]Universités Joseph Fourier-Grenoble 1-CNRS, UMR5183, Laboratoire de Glaciologie et Géophysique de l'Environnement, Saint Martin d'Hères, 38402, France
[4]Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ-IPSL, Gif sur Yvette, 91191, France
[*]now at: Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[**]now at: INERIS, DRC/CARA/CIME, Parc Technologique Alata, BP2, Verneuil-en-Halatte, 60550, France

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## Abstract

Organic Aerosol (OA) measurements were conducted during summer 2008 at an urban background site, in Marseille, France's second city and the largest port in the Mediterranean, an urban industrialized environment known for its active photochemistry. $PM_{2.5}$ was collected using high volume samplers and analyzed for elemental and organic carbon, major ions ($NH_4^+$, $NO_3^-$ and $SO_4^{2-}$), humic-like-substances, organic markers (i.e. primary tracers and $\alpha$-pinene oxidation products), elemental composition and radiocarbon content ($^{14}$C). The real-time chemical characterization of submicron particles was also achieved using a compact time of flight aerosol mass spectrometer. Positive matrix factorization conducted on the organic aerosol mass spectra matrix revealed four factors, including traffic emissions (hydrocarbon-like OA, HOA), industrial emissions, semi-volatile (SV-OOA) and low-volatile (LV-OOA) oxygenated organic aerosol (OOA) related to oxidation processes. The results obtained were in excellent agreement with chemical mass balance source apportionments conducted in conjunction with organic markers and elements. It appears that while primary emissions contributed only 22 % to the total OA (of which 23 % was associated with industrial processes), OOA constituted the overwhelming fraction. Radiocarbon measurements suggest that about 80 % of this fraction was of non-fossil origin, assigned predominantly to biogenic secondary organic aerosol. Non-fossil carbon appears to especially dominate the LV-OOA fraction, an aged long-range-transported OOA, marginally affected by local anthropogenic SOA. We also examined the relation between OOA and $\alpha$-pinene SOA obtained based on the levels of $\alpha$-pinene oxidation products. $\alpha$-pinene SOA showed good correlation with SV-OOA, suggesting that the compounds used for estimating $\alpha$-pinene SOA appear to pertain mainly to the moderately oxidized fraction. In contrast, LV-OOA was found to be intimately related to HUmic LIke substances (HULIS), meaning that these two fractions arise from the same oxidation pathways and share a similar chemical composition (i.e. poly-carboxylic species). A thorough analysis of $\alpha$-pinene individual oxidation products showed that aging can heavily impact their respective concentrations,

as early generation products seem to decay with photochemistry when more oxidized compounds seem to be formed.

# 1 Introduction

Organic Aerosol (OA) constitutes a highly dynamic and complex system governed by multiple emission sources, reversible phase partitioning, chemical transformations and removal (Donahue et al., 2009; Hallquist et al., 2009; Jimenez et al., 2009). A major challenge to our understanding of OA is that organic compounds are extremely reactive in the atmosphere, having gas-phase lifetimes against OH radicals of five to eight hours under typical day-time conditions (e.g. Atkinson and Arey, 2003 and references therein). As a consequence, once emitted (termed Primary Organic Aerosol, POA) or formed in-situ in the atmosphere (termed Secondary Organic Aerosol, SOA), compounds that make up OA will typically undergo one or two generations of oxidation in one day. Recent aerosol mass spectrometer (AMS, Aerodyne) measurements and subsequent positive matrix factorization (PMF2) techniques[1] confirm the prevalence of these aging processes, revealing an overwhelming contribution of highly oxidized compounds (referred to as Oxygenated Organic Aerosol, OOA) (Jimenez et al., 2009). These observations are corroborated by substantial contributions of poly-carboxylic species, termed HULIS (HUmic LIke Substances), ranging between 10 and 50 % of the particulate organic carbon (OC) (Baduel et al., 2010). Depending on the photochemical age of the organic aerosol, this oxygenated fraction is often further deconvolved into two sub-fractions comprising a low volatile highly oxidized OA (LV-OOA) and a semi-volatile less oxidized OA (SV-OOA).

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[1]Positive Matrix Factorization (PMF) applied on AMS-measured-OA is used to deconvolve OA into different factors, subsequently related to different emission sources or processes. Factors often discriminated with AMS/PMF include HOA (Hydrocarbon like OA, from traffic emissions), BBOA (Biomass Burning OA), COA (Cooking OA) and OOA (Oxygenated OA).

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The formation of OOA involves a myriad of different precursors and a great number of reaction pathways, intermediates and products, the detailed characterization of which is beyond the capabilities of current analytical techniques. This immense complexity has led to the development of a two dimensional framework based on AMS/PMF2 results (two dimensional volatility basis set, 2D-VBS), representing the properties of the bulk OA in terms of its volatility and oxidation state (see also Donahue et al., 2012 and reference therein). In this framework, illustrated in Fig.1, the volatility of carbonaceous compounds is first parameterized by the effective saturation concentration ($C^*$ in $\mu$g m$^{-3}$), ranging from $10^{-5}$ to $10^{-1}$ $\mu$g m$^{-3}$ for low volatility matter (e.g. LV-OOA), from 1 to $10^2$ $\mu$g m$^{-3}$ for semi-volatile matter (e.g. SV-OOA and some primary emissions; i.e. HOA and BBOA) and above $10^2$ $\mu$g m$^{-3}$ for volatile organic compounds (VOC) like terpenes and the major part of combustion emissions (Donahue et al., 2009, 2012). Secondly, OA oxidation state is expressed in terms of the O : C ratio (often calculated using AMS data), ranging between almost 0 for un-functionalized hydrocarbons (e.g. HOA) and almost 1 for highly oxidized OC (e.g. LV-OOA) (Aiken et al., 2008). Aging of the organic matter can be represented in this two dimensional space as a decrease in the OA volatility and an increase of its overall O : C ratio, reaching ultimately the oxidation state of LV-OOA.

The same framework makes it possible to investigate the impact of photochemical aging on the molecular composition of OA. Figure 1 presents as an example the aging of $\alpha$-pinene, a precursor of biogenic SOA, widely investigated in chamber experiments (e.g. Hallquist et al., 2009 and reference therein). Represented in this figure are individual compounds identified as first and later generation products of $\alpha$-pinene oxidation (Jaoui et al., 2005; Claeys et al., 2007; Szmigielski et al., 2007) and used as markers to apportion the contributions of $\alpha$-pinene SOA to ambient OA (Kleindienst et al., 2007; Kourtchev et al., 2009, El Haddad et al., 2011b). These products span a wide range of volatilities and oxidation states, ranging from highly volatile compounds (e.g. pinic and pinonic acid) to highly oxygenated low volatility compounds, including tricarboxylic acids and hydroxy dicarboxylic acids with similar properties as the ambient LV-OOA.

Highly oxidized compounds are believed to be formed through the oxidation of early generation products such as pinonic acid (Kourtchev et al., 2009; Müller et al., 2012), even though their formation pathways and their partitioning in the ambient aerosol between SV-OOA and LV-OOA remain at present virtually unknown. In this regard, chamber experiments and chemical transport models tend to underpredict the proportions of this highly oxidized fraction observed in the ambient atmosphere, as shown in Fig. 1 for $\alpha$-pinene SOA (blue and purple contours). This points out a remaining fundamental gap in our understanding of the predominant precursors and pathways controlling the formation and evolution of the highly oxidized fractions (homogeneous oxidation vs. cloud processing and/or heterogeneous reactions) and the role of late generation products in these pathways (Kroll and Seinfeld, 2008; Kroll et al., 2009; Ervens et al., 2011; Monge et al., 2012; Liu et al., 2012). At present, the main precursors of the two OOA fractions in the atmosphere are still also inaccessible using traditional AMS/PMF2 techniques (Heringa et al., 2012 and references therein), hindering for example the discrimination between biogenic and anthropogenic sources. This deficit in our comprehension of OOA formation mechanisms and major precursors is in essence related to the fact that the major constituents of SV-OOA and LV-OOA remain poorly identified at a molecular level.

Within FORMES project (see Favez et al., 2010; El Haddad et al., 2011a, b), a summertime field campaign was conducted at an urban background site, in Marseille (July, 2008), France's second city and the largest port in the Mediterranean. The aim of this campaign was to investigate the predominant sources of OA and its atmospheric aging in an urban industrialized environment, highly impacted by photochemistry. General conditions during this campaign are thoroughly presented in El Haddad et al. (2011a, b), where we demonstrated using a chemical mass balance in conjunction with molecular markers the predominance of SOA. Radiocarbon measurements indicated that this SOA arises mainly from biogenic precursors. The study of biogenic SOA products suggested that non-traditional biogenic precursors and pathways significantly contribute to the formation of this fraction. In this paper, we investigate these precursors and

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pathways based on AMS measurements and PMF2 analysis. The chemical composition, main precursors and evolution of OOA with photochemistry are investigated and linked to the formation and aging of $\alpha$-pinene SOA, a surrogate for biogenic SOA.

## 2  Methodology

### 2.1  Online and offline measurements

Field measurements were conducted during summer 2008 (30 June–14 July), at an urban background site located in a downtown park of Marseille[2]. The area is impacted by fugitive industrial (steel facilities, petrochemical refineries and shipping) and urban emissions, regional transport (see Fig. S1, in the Supplement) and intense photochemistry. The chemical composition of fine PM was investigated every 2 min using a compact time-of-flight (c-TOF, Tofwerk) Aerodyne Aerosol Mass Spectrometer (AMS, Aerodyne). AMS offers real-time measurements of $PM_1$ non-refractory components (OA, $NH_4$, $NO_3$ and $SO_4$, see Fig. S2 in the Supplement) combining thermal vaporization and electron impact ionization (Drewnick et al., 2005). Semi-continuous hourly concentrations of elemental carbon (EC) and organic carbon (OC) in $PM_{2.5}$ were obtained in the field from an OC/EC Sunset field instrument (Sunset Laboratory, Forest Grove, OR, USA; Bae et al., 2004) running at $8\,l\,min^{-1}$. HS-PTRMS High Sensitivity Proton Transfer Reaction Mass Spectrometer (HS-PTRMS, Ionicon Analytic, Lindinger et al., 1998) was deployed to quantify volatile organic compounds (VOCs), with a special focus on isoprene oxidation products (Methacroleine, MACR and Methyl Vinyl Ketone, MVK), tracers of aged biogenic air masses impacting the site. Available data include also 15 min-averaged $NO_x$, $O_3$, $SO_2$ and $PM_{2.5}$ concentrations.

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[2]General conditions encountered, analysis techniques and methodology adapted are developed in the supplementary materials associated with this paper. For more information, the reader can also refer to the following papers: Favez et al. (2010); El Haddad et al. (2011a, b).

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For offline analysis, $PM_{2.5}$ was collected on a 12 h-basis onto prebaked 150mm-diameter quartz fibre filters (Whatman, QMA) using high volume samplers. The carbonaceous content was analyzed for elemental carbon (EC) and (OC) using a Thermo-Optical Transmission method on a Sunset Lab analyzer (Birch and Cary, 1996), following both NIOSH (Schmid et al., 2001) and EUSAAR-2 (Cavalli et al., 2010) protocols. Sample fractions of 11.34 cm$^2$ were extracted into 15 ml ultrapure Milli-Q water by 30 min short vortex agitation for the analyses of major ions ($NH_4^+$, $SO_4^{2-}$, $NO_3^-$), water-soluble organic carbon (WSOC) and water-soluble humic like substances (HULIS). HULIS analysis was performed following the method described in Baduel et al. (2009, 2010), involving an extraction by adsorption onto DEAE resin (GE Healthcare®, Hi-TrapTM DEAE FF, 0.7 cm ID × 2.5 cm length) and subsequent quantification with an OI Analytical 700 total organic carbon analyzer. Fifty elements were measured using ICP-MS (Agilent 7500ce) following complete dissolution of filter aliquots in a mixture of high-purity concentrated HF and $HNO_3$. As fully described in El Haddad et al. (2011a, b) and in the Supplement, a chemical derivatisation/gas chromatography-mass spectrometry (GC-MS) approach was used to quantify primary and secondary organic markers, including α-pinene oxidation products[3], a major focus of this study. The chemical structure of these compounds is shown in Fig. 1. Radiocarbon ($^{14}$C) measurements offer a direct and quantitative discrimination between fossil and non-fossil carbon (Szidat, 2009; Hodzic et al., 2010), as $^{14}$C is depleted in fossil emissions (POA and SOA). $^{14}$C was measured using ARTEMIS Accelerator Mass Spectrometry, following a complete combustion of total carbon (TC = OC + EC) at 850 °C. The modern fraction in TC was determined as the ratio of $^{14}$C / $^{12}$C in aerosol sample compared to $^{14}$C / $^{12}$C in the NBS Oxalic Acid standard (NIST-SRM-4990B).

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[3]α-pinene SOA markers consist of 9 oxidation products, including 3-hydroxyglutaric acid (A1), 3-(2-hydroxyethyl)-2,2-dimethylcyclobutane carboxylic acid (A2), 3-hydroxy-4,4-dimethylglutaric acid (A3), 3-acetylglutaric acid (A4), 3-acetyladipic acid (A5), and 3-isopropylglutaric acid (A6) and 3-methyl-1,2,3-butanetricarboxylic (A7), pinic acid (PA) and pinonic acid (PNA).

## 2.2 Source apportionment

Available data include source contributions to OC apportioned using primary marker's concentrations in conjunction with Chemical Mass Balance (CMB, Watson et al., 1998) analysis, thoroughly described in El Haddad et al. (2011a). Primary sources considered in the CMB comprise vehicular emissions and industrial emissions, the later representing an aggregate of three processes: coke production, metal smelting and shipping/oil burning. Secondary carbon is apportioned indirectly as the fraction of OC non-attributed to primary sources. CMB results are presented comprehensively in El Haddad et al. (2011a) and are used here to constrain AMS/PMF2 outputs (Sect. 3).

$\alpha$-pinene SOA was apportioned using the sum of the concentrations of the 9 markers determined here (Fig. 1) and the marker/OA predetermined in chamber experiments, following the approach developed by Kleindienst et al. (2007).

The AMS organic mass spectra were analyzed using positive matrix factorization (PMF2; Paatero and Tapper, 1994; Ulbrich et al., 2009), which uses multivariate statistical methods to describe the time series of mass spectra as a linear combination of factor mass spectra and their time-dependent intensities. The input matrices (OA mass spectra and uncertainties) were prepared according to the protocol proposed by Ulbrich et al. (2009). Factors provided by the analysis were then related to sources/processes based on their mass spectra, the correlation of their time series with external markers and their diurnal patterns, as shown in Fig. 2 and in the Supplement. The robustness of the obtained solution is assessed by investigating the rotational ambiguity, varying "FPEAK" from −2 to 2, and the influence of the initial conditions "SEEDS" (Supplement). Ultimately, we retained a 4 factor solution, with FPEAK = 0 and SEED = 0 (Fig. 2). Based on the $m/z$ 44 signals in the total OOA (SV-OOA + LV-OOA), O : C ratios of OOA were estimated following the parameterizations proposed by Aiken et al. (2008) and used as a metric of the oxidation state of this fraction.

AMS/PMF2 apportionments and ^{14}C measurements are combined using a multiple regression model to estimate the fossil and the non-fossil contributions to OOA. Details

regarding the approach applied and the related uncertainties and biases can be found in the Supplement.

## 3   OA source apportionment: AMS/PMF2 vs. CMB

OA is apportioned by PMF2 into 4 factors, comprising traffic emissions (termed Hydro-
carbon like OA, HOA), two OOA fractions, SV-OOA and LV-OOA and a fourth factor, unambiguously related to industrial emissions (termed F4), owing to its high correlation with heavy metals (including Pb, Cs, Mo, Fe, La, V, Zn, Ni and Co) and polycyclic aromatic compounds (PAHs, Fig. 2). This factor exhibits remarkable variations similar to that of industrial OA apportioned by CMB, both characterised by episodic ten-fold enhancements in their contributions (Fig. 2), occurring when the measurement site was downwind of the industrial area (El Haddad et al., 2011a). This is a noteworthy result representing an assessment of the overall contribution of OA from industrial emissions, exceedingly complex using common approaches due to the wide variability of processes applied (El Haddad et al., 2011a). This factor contributed on average only 5.1 % of total OA, even in a heavily industrialised area impacted by emissions from metallurgical industries and shipping. In comparison, the CMB model estimates lower contributions for this source (2.3 % of OA), owing most probably to omitted profiles for fugitive industrial emissions in the CMB. Another plausible explanation is that F4 might encompass SOA formed within the industrial emission's plumes during atmospheric transport (El Haddad et al., 2011a), a fraction that is not considered in the CMB to pertain to industrial emissions. HOA is characterised by a prominent diurnal pattern, with increasing contributions during rush hours, correlating with vehicular tracers (EC and $NO_x$, Fig. 2). AMS/PMF2 predicts that HOA contributes appreciable amounts of OA on essentially every day, accounting on average for 18 % of total OA. Slightly lower contributions are estimated by CMB for this emission source (14 % of the total OA), due most likely to some inputs to HOA from sources exhibiting similar mass spectra (see Supplement), e.g. cooking OA (Mohr et al., 2012). The semi volatile fraction of OOA (35.5 % of

OA) shows moderate correlations with nitrate, a semi volatile anthropogenic inorganic component. In contrast, a better correlation is observed between SV-OOA and isoprene gas phase oxidation products (MVK+MACR, see Fig. 2), implying that this fraction is strongly impacted by oxidation products of biogenic precursors. The low volatility fraction of OOA (41.0 % of OA) shows reasonable correlations with sulfate, as a part of sulfate is assigned to primary shipping emissions. Conversely, the correlation between LV-OOA and HULIS is striking, bringing clear evidence that a great part of LV-OOA comprises highly aged poly-carboxylic compounds. Using the approach developed in Aiken et al. (2008), O : C ratios of SV-OOA and LV-OOA are roughly estimated as 0.33 and 0.84, respectively (O : $C_{OOA}$ ∈[0.48–0.72]; Fig. 1), consistent with values reported for these fractions in previous studies (Heald et al., 2010 and references therein).

The result that we want to emphasis is the overwhelming contribution of SOA/OOA (SV-OOA + LV-OOA) predicted by both AMS/PMF2 and CMB, accounting for ∼ 80 % of OA, of which more than half is assigned to LV-OOA. It underlines the predominance of regional transport over primary local emissions (Fig. S1, Supplement). The chemical composition, origin and dynamics of this fraction are discussed in details in the following.

## 4   Fossil vs. non-fossil precursors of OOA

Combining AMS/PMF2 results of Fig. 2 with ^{14}C measurements provides additional insights into the origins and precursors of the 2 OOA fractions, offering a direct and quantitative distinction between their fossil and non-fossil sources (Hodzic et al., 2010 and reference therein). This combination is based on a multiple regression model that reapportioned OA into 6 fractions[4], including HOA, F4, fossil SV-OOA (SV-OOA$_F$), fossil LV-OOA (LV-OOA$_F$), non-fossil SV-OOA (SV-OOA$_F$) and non-fossil LV-OOA (LV-

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[4]All 6 fractions are statistically significant with contributions higher than 0.

OOA$_F$). Results shows that fossil OOA is rather associated with SV-OOA[5], consistent with a fresh OOA locally formed from anthropogenic emissions (Fig. 3). Meanwhile, LV-OOA is quasi-entirely related to non-fossil precursors, in line with an aged, long-range-transported OOA, marginally affected by local anthropogenic sources. The
5  salient feature revealed by such analysis is that non-fossil OOA (or SOA, as pointed out in El Haddad et al., 2011b) governs both OOA fractions, accounting for $80 \pm 8$ %[6] of total OOA, despite extensive industrial and urban emissions. Suggesting that, during summer time when both high biogenic emissions and photochemical processes are present, OOA is mainly attributed to biogenic SOA, this result is inextricably linked
10  to the prevalence of regional transport during the measurement period (see Fig. S1, Supplement). It offers a unique case study to investigate the impact of aging on the evolution of biogenic OOA components, including for example $\alpha$-pinene SOA.

## 5  Link between LV-OOA formation and $\alpha$-pinene SOA aging

### 5.1  Insights into the chemical properties of OOA

15  Based on the concentrations of $\alpha$-pinene oxidation products, $\alpha$-pinene SOA is estimated to contribute on average only 5.1 % of the total non-fossil OOA, suggesting that other precursors and processes are involved in the formation of this fraction (El Haddad et al., 2011b). The link between $\alpha$-pinene SOA and OOA is investigated in Fig. 4. Excluding periods when the site was directly downwind of the industrial area reflected in
20  high contributions from anthropogenic precursors to SV-OOA, $\alpha$-pinene SOA exhibits a good correlation with SV-OOA (Fig. 4). This feature is in line with the correlation of SV-OOA with isoprene gas-phase oxidation products (Fig. 2) and the high proportions

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[5]Note that SV-OOA$_F$ and LV-OOA$_F$ are subjected to substantial uncertainties (see Supplement), hampering their clear discrimination.

[6]The error here (i.e. 8 %) denotes the uncertainties related to this estimation, assessed using a sensitivity test as described in the Supplement.

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of biogenic SOA (Fig. 3). In contrast, LV-OOA does not show any significant correlation with $\alpha$-pinene SOA, in spite of the overwhelming contribution from non-fossil precursors to this fraction (Fig. 3). Taken together, these observations strongly suggest that the compounds used for estimating $\alpha$-pinene SOA appear to pertain mainly to the moderately oxidized fraction (SV-OOA), whereas LV-OOA comprises compounds with a different chemical nature arising from different processes/precursors. In this context, the comparison between the contributions of LV-OOA and HULIS to OA is revealing (Fig. 4), showing an increase of HULIS fraction in OC from 7 to 18 % when the LV-OOA contribution to OA increased from 20 % to 60 %. It should be noted though that the contributions of LV-OOA to OA exceeds by more than three folds the contributions of HULIS to OC, indicating that additional compounds make up LV-OOA. This is consistent with the fact that in general LV-OOA is even more oxidized than HULIS, characterized in our case by an O : C ratio of 0.84, higher than values previously reported for HULIS (O : C$_{HULIS}$ ∈[0.55–0.65]; Graber and Rudich, 2006 and references therein). Other potential candidates believed to contribute to LV-OOA would include a part of dicarboxylic acids characterized by high O : C ratios together with alcohols and their sulfate esters (organosulfates) previously identified as main contributors to SOA, in our conditions (El Haddad et al., 2011b, 2012).

The increase in HULIS contribution is concomitant with a decrease of SV-OOA proportions, an indication that the processes involved in the photochemical aging of SV-OOA into LV-OOA and thereby the oxidation of $\alpha$-pinene first generation products play a central role in the formation of HULIS. The impact of these processes on $\alpha$-pinene oxidation products is investigated below.

## 5.2 Dynamics of $\alpha$-pinene oxidation products with aging

Based on the very principle of the 2D-VBS framework, multiple oxidation steps during atmospheric aging evolving the SV-OOA into LV-OOA are expected to have a strong impact on the distribution of individual $\alpha$-pinene oxidation products. The OOA O : C ratio and the fraction of LV-OOA in OOA is a metric for the degree of oxidation of SOA

components, a quantity that necessarily increases upon oxidation. In our conditions, an increase in the fraction of LV-OOA in OOA from 27 to 78 % represents an increase in the O : C ratio from 0.47 to 0.72 (estimations based on the approach proposed by Aiken et al., 2008). Highly aged OOA, with high contributions of LV-OOA and high
O : C ratios, is likely to be characterized by higher (lower) proportions of later (early) generation products of $\alpha$-pinene oxidation (Fig. 5). The role of multiple oxidation steps on $\alpha$-pinene SOA components is evidenced by the severe depletion of pinonic acid contributions in highly aged OA. The contribution of this early generation product (O : C ratio of 0.3) to the total $\alpha$-pinene SOA decreased from $\sim$12 to $\sim$4 % when the LV-
OOA fraction increased from $\sim$30 to $\sim$80 %. The decay of pinonic acid appears to be concomitant with the formation of the 3 multifunctional later generation products, A4, A5 and A6 (Figs. 1 and 5), a set of compounds with a similar O : C ratio of the average OOA in our condition (0.45–0.70), that exhibited comparable variability during the measurement period ($R^2$>0.9, $n = 26$; Table 1). Their contributions to $\alpha$-pinene
SOA experienced a 3–10 fold increase when the LV-OOA fraction increased from $\sim$30 to $\sim$80 % (Fig. 5). These observations contribute to the growing body of evidence that OA components, in our case $\alpha$-pinene oxidation products and in particular pinonic acid, are highly reactive in the atmosphere, undergoing multiple oxidation steps and forming oxygenated multifunctional compounds. It shows also that in our case SV-OOA and
LV-OOA arise from similar precursors including $\alpha$-pinene, but undergo different extent of aging in the atmosphere changing their chemical properties and dynamics.

The study of the correlations (Table 1) between individual $\alpha$-pinene oxidation products reveals another important set of multifunctional later generation compounds, including A1, A3 and A7. These compounds show relatively moderate correlations
(0.41<$R^2$<0.78, $n = 26$; Table 1) with the less oxygenated compounds of the other set (A4, A5 and A6) and despite their very high O : C ratios (O : C > 0.7, Fig. 1) they do not show any increase with aging. Such an unexpected behaviour remains unexplained at this stage; it might be the outcome of several processes controlling the dynamics of both OOA and $\alpha$-pinene oxidation products, as presented in the following.

1. First, it should be noted that OOA fractions comprise a myriad of compounds derived from a wide range of precursors, while $\alpha$-pinene SOA is only a small fraction of this complex mix. The contribution of other precursors to OOA adds up to the variability of this fraction and complicates its direct comparison with $\alpha$-pinene SOA.

2. Spanning a wide range of O : C ratios (0.3–1) and chemical functionalities (hydroxyl, carbonyl, carboxyl), $\alpha$-pinene oxidation products investigated here are most likely formed over different time scales. Their distribution within $\alpha$-pinene SOA and their correlation with the OOA fractions are thus heavily dependent on the photochemical age of the air masses, the number of oxidation steps undergone, and their formation rate. Thus, the low correlation between $\alpha$-pinene multifunctional oxidation products (A1, A3 and A7) and the LV-OOA fraction might be related to differences in the time scales over which these compounds and those associated with LV-OOA are formed. An element supporting this assumption is that A1, A3 and A7 are characterized by O : C ratios higher than the average O : C ratio of LV-OOA.

3. Current state of the art is that the formation and evolution of $\alpha$-pinene SOA compounds measured here proceed through photochemical reactions with OH radicals, in presence of $NO_x$ (Jaoui et al., 2005; Szmigielski et al., 2007; Kourtchev et al., 2009; Müller et al., 2012). While these processes remain at present poorly characterized, they depend not only on the photochemical age of the air masses (as in point ii) but can be heavily impacted by ambient conditions, such as $NO_x$ concentrations. By modifying the reaction branching ratios, $NO_x$ can influence the distribution of SOA products. Consequently, compounds that are preferentially formed under low $NO_x$ conditions would tend to correlate with a long range transported LV-OOA, whereas compounds that are preferentially formed under high $NO_x$ conditions are likely to be related to a locally formed SV-OOA.

4. Moreover, the concept underlying the approach used here to apportion α-pinene SOA is retrospective in that SOA mass is reconstructed from the concentration of supposedly-conservative specific oxidation products. Further reaction of these products would not only vary their distribution within the OOA fractions but also impact the apportionment of α-pinene SOA mass used as a normalizing entity in Fig. 5. At present, there is a real paucity of data regarding the chemical stability of the markers used here, whilst our findings brought evidence on the aging of pinonic acid in particular, one of the compounds used in the apportionment. Photochemical decay can equally affect later generation products (e.g. A1, A3 and A7) such that their concentrations would not be enhanced with aging, reaching a constantly low steady state. Such poly-carboxylic acids are more likely to be subjected to fragmentation (Baduel et al., 2011; Chacon-Madrid and Donahue, 2011), a key step in the evolution of OOA (Kroll et al., 2009).

5. Still in the context of the marker based approach used here, the oxidation products selected as markers for the apportionment of α-pinene SOA seems to relate overall to moderately oxidized compounds representative of SV-OOA (Fig.4). Hence, α-pinene SOA apportioned using this approach may poorly represent the actual α-pinene SOA and there is a need to include additional more oxidized markers in the apportionment to better capture the variability of LV-OOA.

Indeed, the size of our dataset precludes a clear discrimination amongst the aforementioned assumptions. Further time-resolved measurements of ambient biogenic SOA components with concomitant AMS data are therefore needed to corroborate the trends observed in this study. It would enable a better assessment of biogenic SOA with approaches that does not rely on the markers chemical profiles determined in laboratory studies (e.g. PMF2). A more precise link could be then established between OOA fractions and the formation and aging of biogenic SOA components. Furthermore, it was observed that α-pinene oxidation products determined here seems to relate to the SV-OOA fraction, while the LV-OOA chemical speciation remains poorly characterized,

related generically with HULIS. In this respect, it would be worthwhile to identify with suitable analytical techniques additional later generation products pertaining to HULIS and link their formation with the OOA aging. Finally, we found that aging plays a major role in the decay of early generation oxidation products and the formation of more oxidized compounds. In this regard, further laboratory work is required to provide additional insights into the stability of these products and the pathways involved in their formation and aging.

**Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/19769/2012/ acpd-12-19769-2012-supplement.pdf.**

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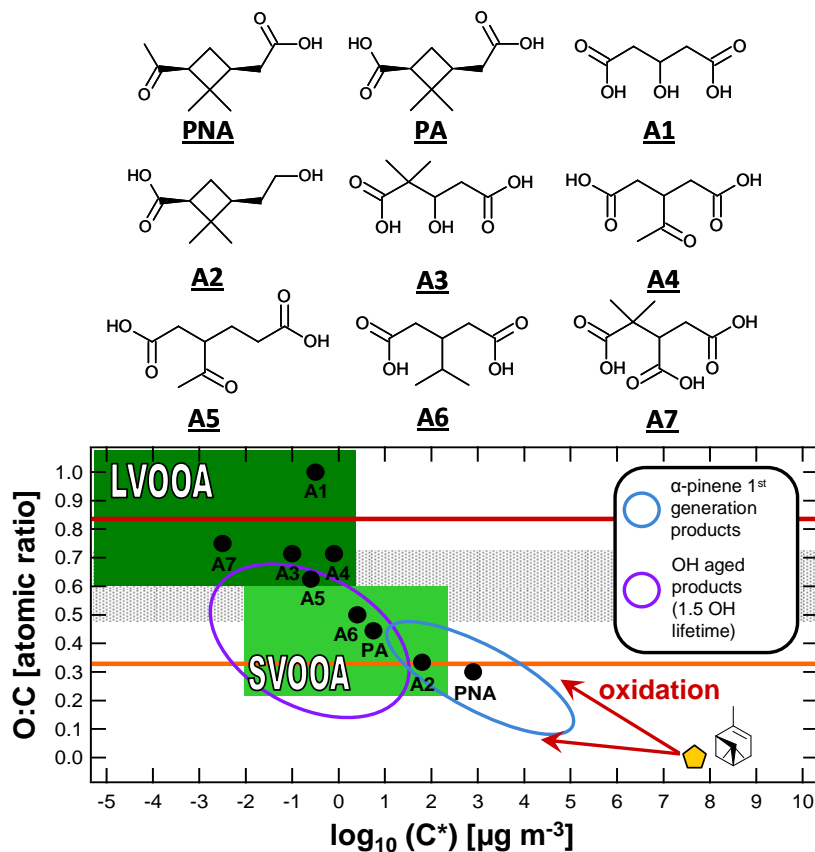
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**Table 1.** Correlation table of α-pinene oxidation products revealing three sets of compounds with similar trends: Set 1 includes PNA, PA, and A2, products formed at the early stages of the reaction. Set 2 includes A4, A5 and A6, products that appear at later stages of the reaction and that show a relative increase with the oxidation state of the aerosol (Fig. 5). Set 3 includes A1, A3 and A7, products that appear at later stages of the reaction but do not show any increase with the oxidation state of the aerosol (Fig. 5).

| $R^2$ | PNA | PA | A1 | A2 | A3 | A4 | A5 | A6 | A7 |
|---|---|---|---|---|---|---|---|---|---|
| PNA | 1.00 | 0.61 | 0.39 | 0.23 | 0.61 | 0.29 | 0.39 | 0.27 | 0.45 |
| PA | | 1.00 | 0.61 | 0.35 | 0.44 | 0.68 | 0.60 | 0.60 | 0.48 |
| A1 | | | 1.00 | 0.36 | 0.72 | 0.72 | 0.74 | 0.77 | 0.86 |
| A2 | | | | 1.00 | 0.37 | 0.48 | 0.57 | 0.43 | 0.32 |
| A3 | | | | | 1.00 | 0.46 | 0.53 | 0.41 | 0.78 |
| A4 | | | | | | 1.00 | 0.92 | 0.95 | 0.65 |
| A5 | | | | | | | 1.00 | 0.93 | 0.69 |
| A6 | | | | | | | | 1.00 | 0.68 |
| A7 | | | | | | | | | 1.00 |

**Fig. 1.** (Caption on next page.)

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**Fig. 1.** 2-D framework for $\alpha$-pinene SOA aging adapted from Jimenez et al. (2009), representing OA oxidation state (approximated by O : C) vs. OA volatility ($\log_{10}(C^*)$ at 298 K). The ambient OOA factors are represented in this 2-D space by the 2 green squares, with LV-OOA being less volatile and more oxidized than SV-OOA. First generation products from $\alpha$-pinene (yellow pentagone) + ozone reaction are distributed according to the blue contour. Products derived from subsequent OH oxidation (1.5 OH lifetimes) of first generation products are represented with purple contour. This oxidation reproduces a substantial shift toward ambient LV-OOA volatility and oxidation state. We added on this 2-D space $\alpha$-pinene first and later generation oxidation products measured in this study by GC/MS (PNA, PA and A1–A7). The volatilities of these compounds are calculated using the approach proposed by Donahue et al., 2012. O : C ratios of pure SV-OOA and LV-OOA retrieved from AMS/PMF2 analysis are calculated following the parameterization proposed in Aiken et al. (2009) and indicated by the orange and dark red lines, respectively. Following the same methodology, the range of O : C ratios ($0.48 < \text{O} : \text{C}_{\text{OOA}} < 0.72$) of total OOA encountered during the measurement period was determined and indicated by the dotted area.
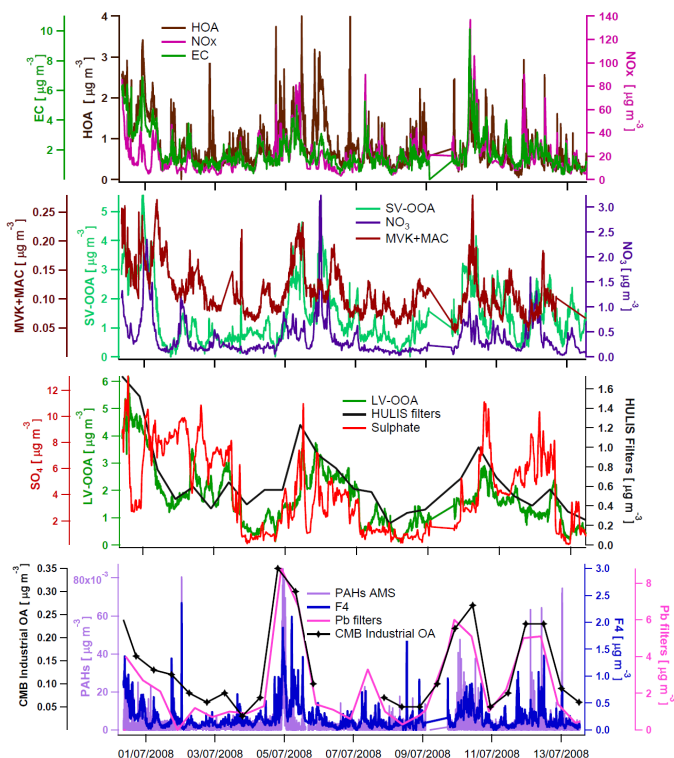
**Fig. 2.** Time series of AMS/PMF2 factors (4 factor solution; FPEAK = 0, SEED = 0) compared with corresponding tracers: $NO_x$ and EC for HOA, $NO_3$ and MACR + MVK for SV-OOA, HULIS and $SO_4$ for LV-OOA and Pb, AMS-PAHs, CMB industrial OA factor for F4.
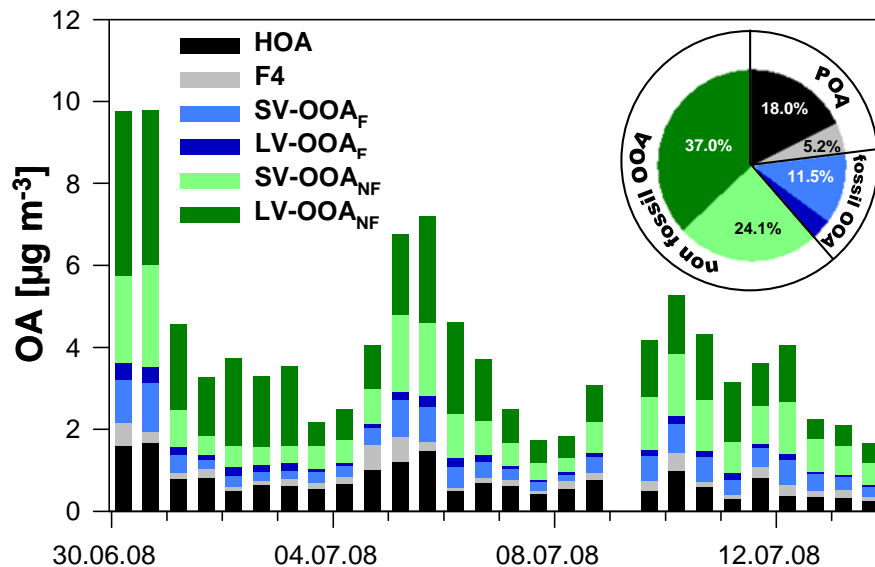
**Fig. 3.** Fossil and non-fossil origins of POA (HOA and industrial OA) and OOA (SV-OOA and LV-OOA) apportioned by combining AMS/PMF2 results with $^{14}$C measurements (see the detailed analysis in the Supplement).
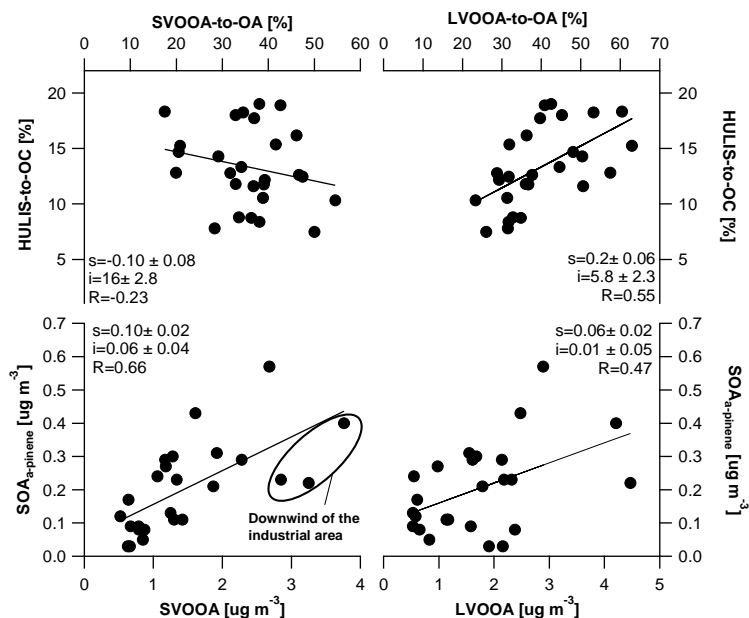
**Fig. 4.** Correlation between the OOA fractions (SV-OOA and LV-OOA) and different SOA fractions, including HULIS and $\alpha$-pinene SOA estimated following the approach proposed in Kleindienst et al. (2007). For $\alpha$-pinene SOA, absolute concentrations [in $\mu g\,m^{-3}$] are compared. Except for periods when the site was downwind of the industrial area and the SV-OOA had high contributions from anthropogenic precursors, $\alpha$-pinene SOA showed high correlation ($R = 0.66$) with the SV-OOA fraction (excluding data points where the site was downwind of industrial emissions would result in a R-value of 0.74). For HULIS, the relative contributions [in %] are compared, because the absolute concentrations of HULIS correlated with both SV-OOA and LV-OOA. The good correlation between HULIS and LV-OOA suggests that a large fraction of LV-OOA comprises poly-carboxylic species that are not well represented by the markers of $\alpha$-pinene SOA.

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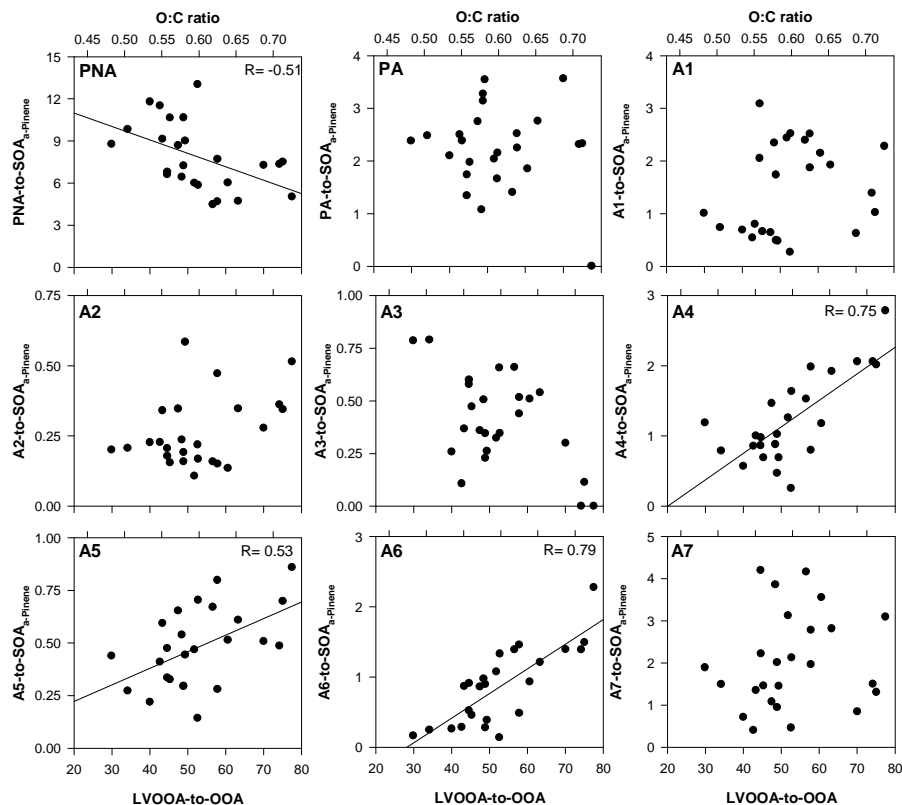
**Fig. 5.** Correlations between LV-OOA-to-OOA contribution [%] and the contribution of each of the α-pinene oxidation products to the total α-pinene SOA [%]. Also shown are the O : C ratios, calculated using the approach proposed in Aiken et al. (2008).

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